COMPARATIVE STUDIES ON EFFECT OF CATIONIC AND ANIONIC FINISHING AGENTS ON SURFACE PROPERTY OF FINISHED LEATHER

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Abstract. The present work attempts to analyse the surface and physical properties of leathers finished with cationic and anionic finishing chemicals. The contact angles of liquid drops resting on the leather surface have been used to evaluate surface energy, acidity, basicity components of the surface energy, polarity and work of adhesion. Contact angle values have been measured for chrome tanned and conventionally re-tanned crust and finished leather made by varying pigment and binder combinations. The wettability of finished leather has been correlated with the contact angle values: the higher the contact angle value the lesser is the wetting observed. Complete wetting can be obtained when the contact angle value is zero i.e. the drop of liquid spreads spontaneously on the surface and partial wetting is obtained when the contact angle value is in between 0and 90^0. Acrylic binders with different film forming properties, protein, polyurethane and butadiene binders have been combined to prepare different finish formulations. The results have been correlated with wet and dry rub fastness, finish adhesion, vamp flexing value, water vapour permeability and water proofness. It has been observed that when the surface of leather is coated with acrylic binder the contact angle value due to polar solvents(water) , non-polar solvents(hexadecane) and moderately polar(DMSO) and methyl iodide show that as the thickness of coating increases, the contact angle value decreases for the base coat and sharply increases when top coat is applied. Top coats have the ability to increase the contact angle and they improve the performance properties of leather such as water resistance, fastness, finish adhesion etc. Cationic and anionic finishing formulations have been compared to study their effect in modifying the surface of finished leather based on contact angle values, wet and dry fastness to circular rubbing and water resistance. It has been observed that leathers finished using anionic finishing technique shows better wet rub fastness and water resistance effect compared to cationic finishing technique.

1 Introduction

The object of finishing is to give a treatment of coatings to the grain surface to protect it against dirt, staining, wetting, mechanical stresses like rubbing, scuffing, flexing etc., levelling or evening out the colour of the grain surface, hiding grain blemishes and upgrading its quality, improving the aesthetic appeal and the sales value of the product. By the finishing process, the grain surface of the leather is coated with various substances and is then submitted to different mechanical operations, depending upon the purpose intended whereby the appearance of leather can be highly influenced to make it more useful, attractive and appealing to users. Finishing may be employed to impart colours, a uniform shade, special patterns, a smooth or grained or printed/embossed surface, lustre (Matt or glossy) as well as opaque (covered) or transparent (aniline/semi-aniline) appearance to the leather surface. Finishing operation is the most vital part of the processing of leather as the final product is judged by its appearance, evenness of colour and surface, feel, handle, break, gloss etc. Hence it is usually the finishers who have to face the complaints or blames, if anything goes wrong. They are also expected to correct whatever faults that have occurred during the earlier operations [1]. Finishing was once considered as an art and was kept a secret but today with the introduction and availability of a wide variety of leather finishing chemicals and mechanisation, finishing is no longer that secret. However, in spite of the innumerable finishing auxiliaries available and marketed by the firms providing details like general composition and properties of the products, mode of application with formulation for different types of finishing of leather, finishing is still dependent upon the finisher's ability of judging and blending of different auxiliaries to make his own combination to give the best finishing effect. Also, he keeps in mind the high qualities required from finishing, like

adhesion, flexibility, durability against weathering and aging, durability against dry and wet rubbing, resistant to pealing, cracking on flexing, light fastness, resistant to the various mechanical operations involved in finishing and permeability to water vapour thus ensuring the hygienic conditions.

The absorption of surface and anchorage and adhesion of finish film can be affected by the surface charge and presence of fatty substances. In the case of chrome tanned crust leathers, the final PH is around 3.5 and this means the surface has cationic residual charge. Most of finishes used in leather finishing are anionic in nature and too much of residual cationic charge may not allow the finish film to anchor well. This combined with the presence of fatty matter will result in poor adhesion of the finish film. The absorptive nature can be assessed by putting a drop of water on the surface and measuring the time taken for absorption. In case, the leather is absorbing less water that means the leather surface may have materials which are hydrophobic. In this case the water contact angle will be more so that the water molecules will form spherical beads rather than spreading on the surface. In which case, traditionally clearing coats are applied to improve the absorptive nature. Clearing coats contain a water miscible solvent like isopropyl alcohol or diacetone alcohol along with a mild alkali like ammonia. The solvent clears the surface fat and ammonia reduces the surface cationic charge on the surface. Sometimes the surface non- uniformity is reduced and made more level by using a dye solution along in which case the coat is called stain coat [2].

When a leather technician wants to make soft leather excessive anchorage is not required because it causes hardening of the surface of leather hence too much clearing coat is counterproductive. In such cases traditionally people use cationic oil ground to seal the surface of the leather so as to avoid excessive sinking of finishing chemicals. This is called sealing coat. In this case we are blocking the absorption of excess chemicals by incorporating the cationic charge on the surface of the leather. Care should be taken to avoid excessive use of the cationic oil ground. Usually 100-150 gram per liter is used to get the optimum effect. When the cationic oil ground is used in excess amount the season coat cannot be adhered properly to the surface of leather, in such case ammonia can be used to reduce the cationic charge. In conventional pigmented leather finishing technique, the natural look and feel of leather is usually lost because of heavy loading of pigments and binders which in turn affect the profitability of a given company. Even though the leather chemical industries are developing different finishing chemicals for up gradation of the surface defects and blemishes, the understanding of effect of each finishing chemicals and auxiliaries on surface and optical property of leather is still limited among leather technicians and researchers. A buyer's first consideration when faced with the leather is probably its feel. "Plastic" finishes with a cold, synthetic feel, or finishes which are too rigid and do not show good levelling and integration with the leather, should be avoided by means of suitable selection from the first phases of making the leather. Efforts to improve the situation on leather already finished are difficult and largely ineffective, even if the wide range of feel modifiers can help.

In this work, the overall objective has been to understand the surface energy parameters of different finishing of leather and relate these properties to the quality of finishing. Further, the work has attempted to optimize the quantity, nature and the combination of different finishing chemicals to obtain optimal finishing properties for different types of leathers.

Thus to quantify the amount of finishing chemicals especially binders and pigment in finishing of shoe upper leather goat crust having similar grain quality were selected and finished by varying the concentration of different binders. Contact angle values were measured for leathers finished with different finish formulations. From contact angle value polar and non-polar component of surface energy, the degree of wetting, work of adhesion were calculated. In addition to this, effects of other finishing chemicals and top coats on the surface and physical properties were also determined. The amount of surface coating applied to the leather influences whether or not the item can be described as genuine leather. If the leather has a surface coating, the mean thickness of this surface layer, however applied, has to be 0.15mm or less, and does not exceed 30% of the total thickness of the leather. The results of this study are especially helpful to develop finishing technology for special type of leathers like water resistance, self-care, light weight and high water vapour permeability and etc.

2 Materials And Methods

The required materials and methods to study the effect of different binder and pigment in surface properties of finished leather were described. The chapter proceeds with the description of characteristics of different commercially available finishing chemicals used for the study. Several finish formulations were prepared to study the surface property of finished leather by varying binders and pigments alternatively and keeping other auxiliaries constant. Contact angle value for different solvents such as water, methyl iodide, DMSO and hexadecane were determined for the respective finish formulations by the help of optical microscope having digital camera mounted perpendicular to the test sample where the drop of solvents going to be applied. The detail procedure for preparation of sample in order to determine contact angle, and the design of the whole experiments were described. The experiments were also conducted to study the advantage and disadvantage of anionic and cationic finishing technique, the effect of pigment to binder ratio on the surface and physical properties of finished leather, film forming properties of different binders, effect of commonly used top coats on the surface of the leather and etc. In addition to this the procedure and methodology to conduct the entire physical tests were also explained.

2.1 Materials

Wet blue leather from goat skin and cow hides were made to be ready for post tanning operation by using conventional post tanning process techniques in order to produce dyed crust leather for finishing process. The leathers which have similar grades were selected for experimental work.

Different finishing chemicals, which are described in the Table 1 and laboratory equipments and instruments (universal testing machine, contact angle measuring instrument, vamp flexing machine, water proofness machine, rub fastness testing machine, water vapour permeability tester, optical microscope, Lastometer, oven, glass wares and glass plates (for film formation) were used.

Table 1. The nature of finishing chemicals used in the experiment.

s/no	Chemical name	Nature	Remarks
1	B1 27047	Medium soft aqueous waxy protein binder	
2	B1 507	Soft protein binder	
3	BM 388-FO	Beauty maker	
4	LW 65416	Clear CAB lacquer water born, hard	
5	HM 51760	Handel modifier, aqueous modified silicon emulsion	
6	HM 51251	Water dilutable silicon emulsion	
7	RA 1216	Very hard acrylic binder	Tg = 53°C
8	B1 27154	Aqueous protein binder	
9	LS 65258	Clear NC lacquer solvent borne	
10	RA 17	Very soft acrylic binder	
11	RA 2354	Medium soft acrylic binder	Tg = -29°C
12	RA 27006	soft acrylic binder	

13	FI 50	Filler wax	
14	PP25824	pigment, brown	
15	PP25884	Pigment, red	
16	WT2586/13886	Water based pu top coat	
17	B1 1370	Aqueous protein binder	
18	XR79053	Water dilutable imine ester crosslinking agent	
19	HM183	Hand modifier, water dilutable silicon emulsion	
20	WT25853/13892	Dull waterborne aliphatic PU dispersion for producing high performance finishes	
21	WT13400	Clear high gloss waterborne acrylic copolymer emulsion	
22	WR 22409	Water repellent, modified polyfluorocarbon emulsion	
23	Lepton aqua top TG	Water based top coat	

2.2 Methods

The methods used to reach at each specific objectives of this study are described in the following sub-titles.

2.2.1 Crust preparation

Thirty pieces of goat wet blue having similar size and grades were purchased from the market. The materials were sammed to remove the excess moisture content and to flatten the surface for subsequent mechanical and chemical operations. Since the materials were designed for production of dyed crust for shoe upper leather, it was shaved with a thickness of 1-1.2mm with strict control to maintain thickness uniformity. After thickness was adjusted, the re-tanning fat-liquoring and dyeing were conducted by conventional post tanning process for shoe upper production.

2.2.2 Finished upper leather preparation

Different finish formulations were prepared by varying concentration and type of pigment and binders alternatively fixing other ingredients constant. Types of Acrylic binders like very soft, soft and medium soft and polyurethane binders have been employed for a given pigment by varying binder concentration. In addition to this different formulation were prepared by using PU binders with or without cross linkers and using some performance chemicals. Finish formulation by using cationic chemicals were also prepared. The formulations were sprayed by using hand spraying machine on crust leather maximum of three coats. As described in the tables below, all the formulations were prepared at the same time and equal volume of the season was sprayed on crust leather having the same area. In all cases three coats were applied in between each coats, the leathers were allowed to be dried to avoid the quality inconsistency.
For anionic finishing technique, different commercially available acrylic resin binders, different PU top coats and cationic finishing chemicals were selected from stahl chemical company for whole experiments and one litre finish formulation were prepared at different p/b ratios by using each a single binder as well as combining the three binders at different p/b ratios. The three resin binders were chosen for experimental work based on their ‘Tg’ values and universal applicability.

Table 2. Finish formulation by using combination of acrylic binders.

Types of chemicals	Finish formulations (gm)					
	F19	F20	F21	F22	F23	F24
Pigment	100	100	100	100	100	100
Vs- resin binder	25	25	25	50	50	50
S- resin binder	25	25	25	50	50	50
Ms- resin binder	50	75	100	150	200	250
Filler Wax	30	30	30	30	30	30
Protein	30	30	30	30	30	30
Water	740	615	660	640	590	540
Total	1000	1000	1000	1000	1000	1000

Note :VS- very soft, S- soft, MS- medium soft

Table 3. Cationic finish formulations.

Chemicals	Finish formulations(quantity in grams)							
	Cat-1a		Cat-1b		Cat-2a		Cat-2b	
	SC	TC	SC	TC	SC	TC	SC	TC
PP 17732	25	-	25	-	50	-	50	-
BI17737	100	-	100	-	100	-	100	-
RU 17702	50	-	50	-	50	-	50	-
FI 1292	25	-	25	-	-	-	-	-
FI 17701	25	-	25	-	75	-	75	-
LW65377	-	100	-	-	-	100		-
FI 77055	-	-	-	-	50	-	50	-
MA 27108	-	-	-	100	-	-		100
Water	500	100	500	100	650	100	650	100

2.3 Finish film formation

Finish films were formed by combining soft and hard acrylic binders with and without protein binder, filler wax and pigments and the tensile strength were measured.

Finish films were formed by using the appropriate substrate for casting the formulations described in Table 3. In this experiment glass plates having 25*15cm dimension were prepared and the calculated amount of formulations were poured on the required area and allowed to dry at 60°C. After the

film were dried the film forming nature of acrylic and protein binders were studied. The dried films were used to determine, young's modulus, elongation, tensile strength and contact angle.

2.3.1 Finish film tensile strength determination

Glass plates having dimensions 25cm by 15cm have prepared and different binder combinations with known volume were poured uniformly and film forming nature of different binders and binder combinations were studied. The samples have allowed drying at room temperature for tensile strength measurement. After the films have dried the samples were prepared by cutting with 10mm width in the direction along the glass plate and across the glass plate. The thickness of the film sample is measured at five different points and the average value has taken for calculation. The tensile strength and percentage elongation have been tested by using Instron universal testing machine by setting the clip pressure of 3 bars and testing speed of 100mm/min for all samples.

$$tensilestrength = load/area \text{ where, } Area = width \times thickness$$

2.4 Adhesion of finish test /SATRA TM 411 sole bond test

This test is intended to determine the strength of finish adhesion to the leather surface. Force required pulling the leather away from its surface finish layer, the force being applied steadily at an angle of about 90^{o} to a rigid adherent plate to which the finished side of the leather has been bonded. The finished side of a strip of leather is bonded to a PVC plate by means of heat activated adhesive film. Force was applied to the free end of the strip to peel the leather from the finish over a distance and measured by using universal testing machine.

2.5 Flexing endurance of finished leathers: SATRA 25:1992/BALLY TM 55

Flexing endurance is one of the wear properties of leather. If leather surface coating (finish) is not properly applied with correct proportions and following all technical procedures, the finish surface upon bending repeatedly develops cracks, flaking, brittle and delamination.

For all the finish formulations prepared by varying the concentration and type of resin binder, both wet and dry flexing endurance test were conducted. The tests were performed by the machine called vamp flexing machine. In performing the test first the test specimens were folded along the longer sides so that the finish side facing inward and one end of the folded specimen were clamped in upper clamp and the other end was clamped on lower clamp. The tests were conducted based on the above standard. For dry flexing test, the test specimens were flexed for 10,000 and 500,000 flexes and the finish damage were observed by magnifying glass and the type of damage were recorded. For wet flexing endurance test, first the test specimen was gently immersed in to water for approximately 30 seconds prior to clamping it on to the machine. The test specimen was clamped on to the machine in similar way to that of dry flexing but the number of flexing was adjusted for 10000 and 100000 flexes based on the above standard and the finish damage observed were assessed experienced expert with help of magnifying glass and the type of damage were recorded**.**

2.6 Color fastness to circular rubbing - SATRA TM 8:1992

2.6.1 Dry Rub Test

The test specimen was cut about 75mm square from the finished leather. And the specimen was placed on the horizontal platform and a felt pad was secured on the spindle and brought in contact with the test specimen. The weight was adjusted to 24.5±0.5N and the machine was operated for 512 revolutions. After the required revolutions were completed, the leather and the felt pad were removed from the machine. To assess the colour change and transfer of colour (degree of staining)

standard grey scales were used. The number of cycles and the colour change and colour transfer depend up on the type of leather and customer's requirement**.**

2.6.2 Wet Rub Test

Clean white felt pad was immersed in cold water and boiled until all the felts are completely wetted. After complete wetting, the felts were allowed to be cooled. The felts were removed one by one and excess water was slightly squeezed out prior to attaching it to spindle. The loads were adjusted to 7.1N forces. The spindle was brought into contact with leather specimen for 60 seconds and the machine was allowed to operate for 256 cycles and the colour change and colour transfer form test piece to felt pad was assessed based on the grey scale.

2.7 Water vapour permeability – ISO 14268/IUP15/EN 20344

Water vapour permeability is the unique property of leather. Under normal conditions about 5 grams/hour sweat is produced by a human when the atmospheric condition is between 30-35^{o}C. Under industrial working condition, the sweat produced by a human foot is around 10 gram/hour. This sweat has to be sent out to the outside of the shoe for comfort wear. Leather footwear has the ability to absorb the sweat produced and transmit to the upper part of the leather through wicking process. Once it reaches the upper surface, the sweat evaporates into atmosphere. This process is known as Water vapour permeability or water vapour transmission. This is possible by the porosity characteristic of leather. Filling, finishing and fat liquoring processes in leather making reduces this water vapour transmission property to a greater extent.

Based on the above standards

Water vapour permeability (wvp), mg/cm^2/hr is equal to:

$$Wvp = \frac{7\,640XW}{dxdxt}$$

Where, w is the mass difference in mg $W= w1\text{-}wo$

W0 is initial mass of the leather and the dried silica jells.
W1 is the final masses after the moisture from the leather is transmitted to silica jell within 8 hrs.
d is the diameter of the leather sample in mm
t is the time in taken for moisture transmission form water to silica jell

2.8 Determination of water resistant property, SATRA/ STM 606D

A test piece were formed into the shape of a trough and flexed whilst partially immersed in water. The time taken for water to penetrate through the test piece is measured. The method also allows the percentage mass of water absorbed and the mass of water transmitted through the test piece to be determined. In addition to this the time taken for penetration of water through the cross-section was determined. In this experiment percentage water absorption and the time taken for water to penetrate to the cross-section were determined for shoe upper leather finished with different PU based binder combinations and cationic binders.

2.9 Determination of contact angle

Contact angle is very important technique to understand wettability of polymeric surface up on different polar solvents and non polar solvents. Three solvents are usually used for contact angle measurements

which are water (highly polar), DMSO (moderately polar) and hexadecane (non polar).The contact angle values will vary based on the type of coating when a drop of these solvents are applied on the surface of finished leather by using micropipette, the drop position were adjusted, and the contact angle picture were taken by using the camera which is mounted on the microscope. For all the contact angle measurement, the following instruments were used.

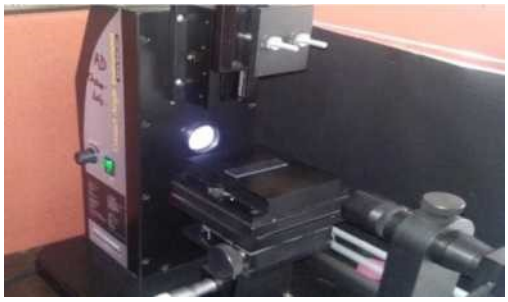

Figure 1. Contact angle instrument.

2.9.1 Contact angle for the crust leather

The crust sample was cut into appropriate rectangular shape with size similar to microscopic slide with dimension of 3cm by 1cm. The contact angle for the dyed crust leather was measured with the help of contact angle measuring instrument described in Fig. 1. By using three different solvents highly polar (water), medium polar (methyl iodide) and completely non-polar (hexadecane) contact angle value were measured and recorded

2.9.2 Determination of contact angle for binders

Different binders were coated on microscopic slid and allowed to dry completely in the desiccators. After the coating has dried, the contact angle was determined by the help of the instrument described above similarly three different solvents were used i.e. water, hexadecane and methyl iodide and the values were recorded.

2.9.3 Determination of contact angle for finish formulations

Different finish formulations were prepared and applied on crust leather by using hand spray technique and the samples have prepared similarly and the contact angle have been determined similarly with the above solvents and the values have noted.

2.10 Surface energy calculation

By using young's equation, the surface energy of any solids can be calculated from the contact angle value.

Surface energy of chrome crust leather can be calculated as follows

$$ylv(\ 1 + cosO) = 2\ [jysv^{d}ylv^{d} + \text{^}ysvPylv^{p}] \text{---------- ----------} (1)$$

Where 9= contact angle yfp=liquid- vapour surface energy

ysv^{d}=solid- vapour interfacial energy of non polar component ylv^{d}=*liquid-* vapour interfacial tension of non polar solvent ysp^{p}=solid- vapour interfacial energy of polar component ylv^{p} =Liquid- vapour interfacial energy of polar component

In this experiment, two liquids were used to calculate the polar and non-polar component of surface energy, water and hexadecane respectively.

In order to calculate Non polar component of surface energy, the polar component in equation [1] will vanished and the equation will be reduced to the form:

ylv(1 + ***cos0) =*** 2 ***[^ysv^{d}ylv^d***----------(2)

By rearranging terms, the non polar component of surface energy, ysp^d can be expressed as

H rniv(l+cosQ)^2

Ysv^a = ----------(3)

Where, 9 is contact angle For hexadecane, ***ylv = 27.47mN/m*** Hence, equation [3] reduced to

ysv^a =-L_-***L.***----------(4)

By combining equations [3] and [4], the polar component of surface energy, ***®sv^p*** can be calculated as follows:

[Ylv(l+cosS)_ ^ y$_{sv}$dyi$_v$d] 2

ySV^p = - ----------(5)

mivP

Where, 5= contact angle

ylv= total surface tension of liquid

ylv^d = non polar component of surface tension Value for a given liquid ***ylv^p = polar component of sufrace tension for a given liquid***

For water, the total, polar and non-polar surface tension values are given in literature these are:

ylv= 72.8mN/m ***ylv^d = 21.8mN /m ylv^p = 51mN fm***

By substituting the above surface tension values for water and non-polar component of surface energy value,'***ysv^d*** obtained by using equation [4], the polar component of surface energy for the given solid material i.e. leather can be calculated and equation [5] can be reduced to:

$$ysv^p = \frac{72.8(l+COs5)}{2} - \frac{\blacksquare 2\hat{}ysv^d * 21.8]^2}{51} \quad \text{----------(6)}$$

Here, cos5 value will vary based on the water contact angle, 5 and ***ysv^d*** depend on the hexadecane contact angle value, 9

Therefore it is possible to calculate the polar and non-polar component of surface energy values by using equation [6] and [4] respectively.

And the total surface energy, ysv will be the sum of polar and non-polar components, i.e.

ysv = ysv^d + ysv^p----------(7)

Van Oss- Chaudhury- Good (OCG) thermodynamic approach can also be used to determine the surface free energy components of solids.

A similar comparison can be made by considering the Van Oss, Chaudhury and Good (OCG) model [13] in which the solid/liquid work of adhesion is expressed as a sum of three terms:

In these approach, the polar component of surface ***energy,ysv^p*** is expressed in the form of two components i.e. Lewis acid and Lewis base ***(ys+and ys$^-$)*** parameters respectively. To calculate these values in these experiments, three liquids such as water, hexadecane and di-methyl sulfoxide (DMSO) were used.

yL(1 + cos0) = 2^ys^{LW}yL^{LW} + 2-^ys+yl$^-$ + 2^ys$^-$yl+----------(8)

Where 9= contact angle yfp=liquid- vapour surface energy

ys^{LW} = the Lifshitz-van der Waals (non-polar) component of the surface free energy ***ys***+Andys$^-$= the Lewis acid parameter and the Lewis base parameter, respectively.

From the contact angles of at least three liquids of known surface tension parameters ***(yL,ys^{LW}/ysv^d,yl+and yl$^-$)*** equation (8) can be used to determine the van Oss, Chaudhury and Good parameters for the surface free energy of the solid.

Thus, by considering three polar liquids, it is theoretically possible to determine the Lifshitz-Van Der Waals (non-polar) component, YS^{LW} of the surface free energy of polymers. This result can be compared to the value obtained with the equation (2)

$$yL(l + \cos 0) = 2\hat{}ys^{LW}yL^{LW} \quad \text{----------(9)}$$

Equation 2) can be used for determination of non- polar component of surface energy by using the contact angle of non-polar liquids such as hexadecane, di-iodomethane, a-bromonaphthalene and etc. In this paper contact angle and surface tension values of water and DMSO were used as polar liquids. By using these values it is possible to determine the Lewis acid and Lewis base parameters of surface energy of the given liquid this in turn help to know the charge characteristics of the surface of the given finished leather [13].and it can be expressed as a square root of geometric mean of the Lewis acid(ys+ and Lewis base (ys^-) parameters [1]. Mathematically:

$$ysv^p = 2\hat{}ys+ys\tilde{} \quad \text{----------(10)}$$

3 Results And Discussion

3.1 Contact angle and surface energy value for dyed crust and different finish formulations.

The crust sample was cut into appropriate rectangular shape with size similar to microscopic slide i.e. 3cm by 1cm. The contact angle for the dyed crust was measured with the help of contact angle measuring instrument which is microscope where digital camera is mounted on it to take the droplet pictures on the test specimen. Three different solvents highly polar (water), less polar (methyl iodide) and completely non-polar (hexadecane) have chosen and the values were described as follows:

Table 4. Contact angle values for crust leather for shoe upper (black)

Sample no.	Contact angle values			Remarks
	WCA	MICA	HDCA	
B1	69.01	ND	ND	In each cases one drop of the solvents (approximately **5pl**) were applied
B2	80.69	ND	ND	
B3	80.66	ND	ND	
B4	66.02	ND	ND	
B5	85.61	ND	ND	
B6	73.47	ND	ND	
B7	78.12	ND	ND	
B8	83.59	ND	ND	
B9	62.43	ND	ND	
Average	75.51	-	-	

ND=not detectable

From table II one can conclude that the surface contact angle with less polar solvent (methyl-iodide) and non polar solvent (hexadecane) for the crust leather is negligible i.e. the drop of the liquid was spontaneously dispersed on the surface of the leather this might be due to the imbalance between

the solid - liquid interfacial energy and the cohesive force of the molecules of the solvents. But in the case of water the contact angle is approximately more than 75°C which is indication of hydrophobic nature of the given leather. The cohesive force which is due to the interaction of the molecules of water/surface tension of water is more than the solid- liquid (leather surface/water) interaction. Therefore the molecule of water tends to form droplets rather than spontaneously spreading as it was observed in the case of methyl iodide and hexadecane. The higher value of the contact angle indicates the slower wettability of the surface by respective liquids in contact with the surface.

By using equation [1], it is possible to determine the surface energy of crust leather and finished leather finished with different finish formulations as follows. As it has described in table-II above, the average value of contact angle for the crust leather is 75.51 in degrees. By using equation [1], it is possible to calculate polar and non polar components of surface energy and hence total surface energy. For the surface energy calculation, contact angle for water and hexadecane were used.

3.2 Surface energy calculation for two liquid systems

Consider the contact angle for hexadecane to be zero and for water to be 75.51°

0 of water=75.51^0

0 of hexadecane=0^0

ylv for water=72.8mN/m

ylv for hexadecane= 27.47mN/m

It is possible to calculate the total surface energy by using equation (3.1) as follows:

ylv(1 + ***cosO***) = 2 [V ***ysv^{d}ylv^d + jysvPylvP]***

In the case of hexadecane, the polar component will be vanished because it is highly nonpolar substance, therefore; The above equation becomes:

ylv(1 + ***cos0) =*** 2 ***[Vysv^{d}ylv^d***

27.47mN/m (1+cos0)=2[Vysv^d * ***27A7mN/m*** By rearranging the values

ysv^d=27.47m N/m

In similar way, the polar component of surface energy(Hsp^p)can be calculated, by considering the contact angle value of water and its polar and non polar component of surface tension values as follows:

ylv(l + cos0) = 2 [V ysv^{d}ylv^d + VysvPylvP

By substituting the values

72.***8mN/m(l + cos7S.*** 81) = 2+ ***-^ysW **** 51mN/m]

By rearranging terms, the polar component of surface energy will be:

ysp^p = 8.53m N/m

From the polar(ysp^p) and non polar(ysv^d) component of surface energy values one can see that there is inverse relationship between surface energy and contact angle i.e. the higher contact angle the smaller the surface energy and vice versa.

The total surface energy of the solid material (crust leather) is the sum of polar and non polar components.

ysv= ***ysv^p*** +ysp^d=8.53m N/m+27.47m N/m=36m N/m

The above surface energy value is the specific for the particular crust leather taken for the control. The magnitude will vary based on the type of re-tanning and fat-liqouring chemicals used. Any surface treatments like coating and different mechanical operations have significant influence on the surface energy.

Figure 2. Water contact angle values on crust leather.

Effect of different leather finishing chemicals like binders, pigments, fillers, waxes, top coats and feel modifiers have significant influence on the magnitude of surface energy values. It has been observed that the surface energy parameter value was reduced by finishing the given crust leather by the help of different pigments and binder combinations and other leather finishing ingredients. By using the contact angle value of hexadecane and water with the finished leather the surface energy for each binder pigment combinations applied on the surface of leather, individual binders coated and dried on the microscopic slide and different finish films have been calculated.

Table 5. Effect of cationic oil ground on contact angle value.

Specimen	Type of solvents			surface energy		
	0 of Water	0 of methyl iodide	0 of Hexadecane	*ySpd*	*ySpP*	*ysv*
1	98.51	46.95	63.15	14.48	3.46	17.94
2	98.48	55.43	63.16	14.48	3.47	17.95
3	104.48	55.69	70.62	12.19	2.38	14.58
Average	100.51	52.69	65.64	3.71	3.06	16.75

From Table 5 it is evident that the contact angle value is increased because of the oil ground used at the very beginning of the finishing operation. This hinders the excessive sinking of finishing season whenever the absorptive nature of leather is very highthis in turn reduces the wettability of the surface. This technique is applicable whenever there is excessive sinking of finishing chemicals if the crust leather is too absorptive which can affect the natural look of the leather to be finished. The amount of oil ground used has to be optimum i.e. 100-150gram per 1000ml of Sealing coat mixture. If it is beyond this range there might be poor adhesion of the season since the water contact angle will be much far from 90°. Therefore the finishing technician has to control excessive use of oil ground.

Table 6. Determination of water resistance of flexible leather.

S.No	Formulation name Water resistance of flexible leather	% Water absorption	Penetration time(min)
1	PUT1A	64.4	13.7
2	PUT2A	42.3	54.3
3	PUT3A	91.7	3.5
4	PUT4A	87.7	4.6
5	PUT5A	69.0	53.4

6	PUT6A	61.2	4.4
7	PUT1	111.1	24.5
8	PUT2	87.7	23.0
9	PUT3	116.1	15.7
10	PUT4	100.7	10.1
11	PUT5	81.4	23.2
12	PUT6	95.0	9.4
13	Cat-1a	129.2	1.2
14	Cat-2a	128.9	0.4
15	Cat-1b	158.5	0
16	Cat-2b	109.0	0.4
17	ccat	161.6	0

Note: ccat is control dyed crust

From the table one can deduce that percentage water absorption is more in the case of cationic finishing technique. In addition to this water was penetrated immediately to the cross section of the leather finished with formulations cat-1a, cat-2a cat-3a and cat-4a and hence the water resistance effect is poor. As it has explained in determination of contact angle value, the value is lower as compared with all other anionic finishing techniques. Almost no difference in percentage water absorption was observed as compared with the control crust. From this result one can conclude that cationic finishing technique is not suitable to improve the water resistance effect and other performance properties but the main advantage of cationic finishing is to get good covering effect without affecting the natural look, flexibility and softness.

3.3 Rub fastness result for cationic finish

Poor colour fastness to circular rubbing was observed in the table below in the case of cationic finishing this is because of the cationic nature of chrome tanned crust. Since the charge of the substrate/crust and the charge of cationic finishing chemicals have similar nature, the chemicals are loosely bound to the surface of the leather.

Table 7. Rub fastness result for leather finished with cationic finishing technique.

Specimen	**Formulation name**	**Colour fastness to circular rubbing**	
		Dry at 512 cycles Felt pad	Wet at 256 cycles Felt pad
1	Cat-1a	3	1
2	Cat-2a	3	1/2
3	Cat-1b	3	1/2
4	Cat-2b	3	1

4 Conclusion

Contact angle was used as a parameter to study the effect of each finish formulations on the surface property of the leather. Water, methyl iodide, hexadecane and DMSO were used to measure the liquid-solid contact angle. The experimental result from contact angle value showed that coating with pigments and binders have increased the contact angle value compared to the control crust. And the corresponding value of surface energy were calculated by using Thomas young equation and the results showed that there is decrease in surface energy when the contact angle increases. It was observed that when the contact angle increases the degree of adhesion and the wettability of the surface of the leather were decreased. In addition to this the effect of top coats and other finishing auxiliaries other than pigments and binders on contact angle value were investigated. Fillers have the ability to increase the contact angle.CAB top coated leather showed more contact angle than PU and acrylic top coats. This value clearly showed that wettability is more in the case of PU and acrylic top coated leathers than CAB top coated leathers.

The effect of number of top coats on water contact angle value were determined ,and the experiment showed that the value were decreased gradually at the beginning of the coat because the top coats are water based so during the coating process the hydrophobic nature of the surface of chrome tanned leather have decreased. And finally the contact angle value were increased and the corresponding surface energy were reduced when CAB top coat were sprayed. In general when the coating chemicals have more polar groups the contact angle values were observed to be increased.

Physical tests like rub fastness, finish adhesion, water vapour permeability and flexing endurance were conducted for leather samples finished with different acrylic binder pigment combination, cationic finish formulations and PU binders with and without incorporation of performance chemicals. The physical test results showed that pigment binder ratio and the property of the given binder have significantly affected the above mentioned physical test parameters. In the case of acrylic binder-pigment combination better result were obtained when we use combination of soft, medium soft and very soft binders at 1 to 3 p/b ratios but very soft binder has to be used in smaller proportion to minimize the tackiness effect. And better wet rub fastness and water resistance effects were observed in the case of acrylic resin finish and PU based finishing technique compared to cationic finishing technique.

Film forming property of different acrylic binders and protein binders were studied and the result showed that soft, medium soft and very soft acrylic binders form flexible, softer films and hard acrylic binders do not form film at room temperature whereas protein binders form discontinuous and brittle film.

The wettability of the surface of leather has to be good before applying the top coat otherwise the top coat cannot adhere to the surface of the leather whenever such hard binder is used at the base coat in larger proportion. Resin binders having lower water contact angle are ideal for base coat since they can easily spread on the surface of the leather this in turn facilitates degree of adhesion.

Compared to anionic finishing, cationic finishing chemicals are shows less contact angle with water and hence more wettable and poor fastness properties. Improving the performance properties such as fastness, water absorption and etc. of cationic finishing technique is open for further research and development.

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References

1. *S.S.DUTTA In introduction to the principle of leather manufacture (Fourth edition),*
2. *N.K.Dr. Chandrababu. Manual on principle of leather finishing (unpublished), CLRI, India*
3. *Synthetic Resins & Leather Finish. www.aaqtic.org.ar/congresos/china2009/download/2-4/2-152.pdf*
4. *J.H Sharphouse, Leather Technician's Hand book.*
5. *S.V.Kanth, , B.Madhan, R.Venba and A.Dhathathreyan. Effect of different re-tanning systems on surface properties of leather. JALCA, VOL, 102, 2007.*
6. *D.Y. Kwok, A.W. Neumann, Contact angle measurement and contact angle interpretation, Advances in Colloid and Interface Science81 (1999) 167-249.*
7. *Journal of achievements in materials and manufacturing engineering. Methods for calculation of surface free energy of solids.Vol.24, Sep. 2007*
8. *K. B. GilleoSheldahl, Inc. Rheology and Surface Chemistry*
9. *Van OSS, C.J. and R.F. Giese, colloid and surface properties of clay materials and related minerals. New York, 2002. Marcel Dekker.*
10. *Norris, J.G. surface free energy of smectite clay materials, in SUNY, 1993: Buffalo*
11. *P. F. Rios 1, H. Dodiuk1, S. Kenig1, S. Mccarthy2 and A. Dotan1.The effect of polymer surface on the wetting and adhesion of liquid systems. Vol. 21, No. 3-4, pp.227 - 241 (2007)*
12. *A. W. Adamson, Physical Chemistry of Surfaces, 5th edn. Wiley, New York, NY (1990).*
13. *ALAIN CARRE, Polar interactions at liquid/polymer interfaces, J. Adhesion Sci. Technology., Vol. 21, No. 10, pp. 961-981 (2007)*
14. *Henry Fleming Payne, "Organic Coating Technology", Vol. 1, John Wiley & Sons, Inc., USA, 1954*
15. *Colour quantification based on CIE guideline, European association of flat glass manufacturers, January 2005.*
16. *Kryszt of Bienkiewicj, "Physical Chemistry of Leather Making", Robert E. Krieger Publishing Company, Florida, 1983.*
17. *Kinloch, A.J., "Adhesion and Adhesives - Science and Technology", Chapman and Hall, 1987*
18. *Heidemann, E., "Fundamentals of Leather Manufacture", Edward Roether Ed., Darmstadt*
19. *Sthal chemical company, Leather International., Cationic finishing technology: October 2002.*
20. *Saimani Sundara, NarasimanVijayalakshmia, Sanjeev Gupta b, R. Rajaramc, Ganga Radhakrishnan. Aqueous dispersions of polyurethane-polyvinyl pyridine cationomers and their application as binder in base coat for leather finishing. Progress in Organic Coatings. Vol.56, page 178-184, July.2006.*